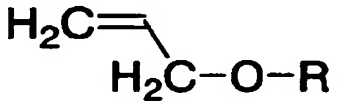
[Document Name] SPECIFICATION

[Title of the Invention] FLUORINE-CONTAINING ALLYL ETHER COMPOUNDS

[Scope of Claims]

[Claim 1] A fluorine-containing allyl ether compound represented by the following general formula 1.

[Chem. 1]



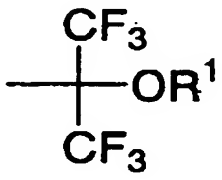
(1)

(In the formula, R represents an organic group containing at least one fluorine atom and having an alicyclic structure.)

[Claim 2] A fluorine-containing allyl ether compound, which is characterized in that the alicyclic structure of R in the allyl ether according to claim 1 is an alicyclic structure containing a cyclohexane structure or bicyclo[2.2.1]heptane structure.

[Claim 3] A fluorine-containing allyl ether compound, which is characterized in that R in the allyl ether according to claim 1 or claim 2 contains a hexafluoroisopropanol or unit derived therefrom, which is represented by the following general formula 2.

[Chem. 2]



(2)

(In the formula, R^1 is a hydrogen or alkyl group of a carbon atom number from 1 to 6 and optionally contains a heteroatom such as oxygen.)

[Detailed Description of the Invention]

The present invention relates to fluorine-containing allyl ether compounds, which are useful as raw material monomers of polymer compounds.

[0002]

[Prior Art]

In recent years, as demands for finer semiconductors have been increasing, there have been conducting active developments of next generation lithography technology using shorter wavelength light sources (for example, see Non-patent Publication 1). In the developments of such next generation lithography, the resist material development is one of those holding important positions. Now, a major type of resist is a positive-type resist material, in which an acid generated by light irradiation is used as a catalyst and then solubility of the resin in alkali is increased along with a chemical change of the resin by the acid. However, in the trend toward such shorter wavelength of light, there are problems that novolak resins, acrylic resins, styrene resins and the like, which are used in current resists are insufficient in transparency.

[0003]

[Non-patent Publication 1]

Y. Kamon et al., J. Photopolym. Sci. Technol., 15, 535 (2002).

[0004]

[Task to be solved by the Invention]

It is a task of the present invention to provide a monomer that can become a raw material of resist materials and base polymers for optical materials, which are required to be low in light scattering and absorption and high in transparency.

[0005]

[Means for solving the Task]

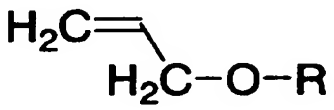
Acrylic resins and styrene resins that have been used in the past for resist materials have high light absorption derived from their containment of a structure such as carbonyl group and aromatic ring. In contrast, the present inventors found a novel fluorine-containing allyl ether, which is useful as a raw material monomer of highly transparent fluorine-containing copolymers.

[0006]

That is, the present invention provides an allyl ether compound represented by the following general formula (1).

[0007]

[Chem. 3]



(1)

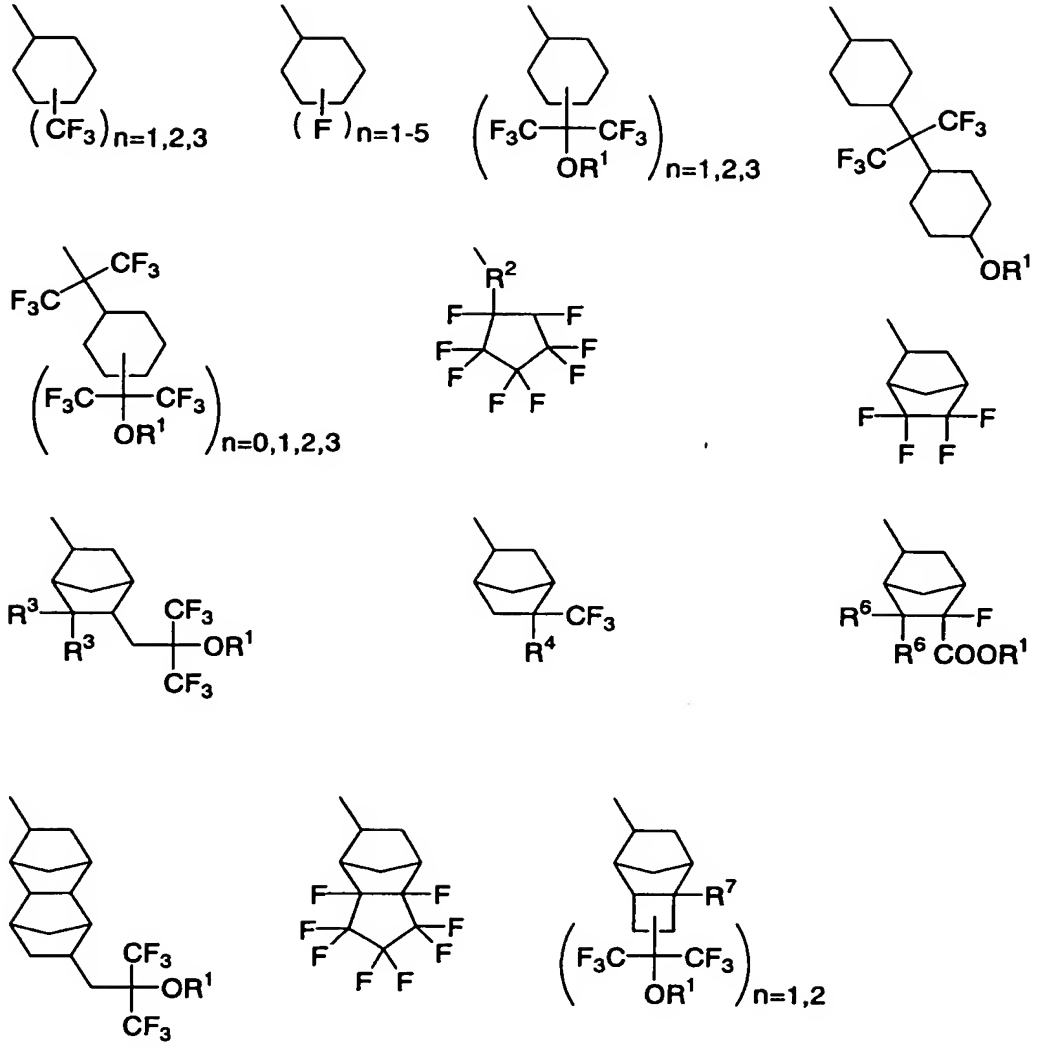
(In the formula, R represents an organic group containing at least one fluorine atom and having an alicyclic structure.)

[0008]

In the following, the present invention is explained in detail. A fluorine-containing allyl ether compound of the present invention is represented by the general formula (1). In the general formula (1), R is an organic group and is characterized in containing at least one fluorine atom and having an alicyclic structure. Herein, the alicyclic structure may be a single ring such as cyclohexyl or a multi-ring such as a skeleton derived from bicyclo[2.2.1]heptane, tricyclo[5.2.1.$0^{2,6}$]decane, tetracyclo[4.4.0.$1^{2,5}$.$1^{7,10}$]dodecane and the like. Furthermore, it may contain a reactive group or the like that is released by the action of acid. As those organic groups are specifically exemplified, those of the following structural formulas are cited.

[0009]

[Chem. 4]



R^1: H or an alkyl group of C=1-6 and may contain a hetero atom such as oxygen;

R^2: an alkyl group of C=0-5;

R^3: H or F;

R^4: CF_3, OH, CO_2H, CO_2R^5 or $OCOR^5$ (R^5: an alkyl group of C=1-6);

R^6: H or F; and

R^7: H or an alkyl group of C=1-5.

[0010]

Of these, the allyl ethers containing structures, such as cyclohexane and bicyclo[2.2.1]heptane, in their alicyclic structures are preferable as monomers for resist materials, since light absorption derived from a double bond is low in case that they turn into polymers and since the polymers are superior in heat resistance. A hexafluoroisopropanol unit (-$C(CF_3)_2$-OH) or hexafluoroisopropanol derivative unit (-$C(CF_3)_2$-OR^1, where R^1 is a hydrogen or alkyl group of a carbon atom number of from 1 to 6 and may contain a hetero atom(s) such as oxygen) in the allyl ether serves to improve adhesion of the polymer to substrate.

[0011]

Various known processes can be used for producing a fluorine-containing allyl ether of the present invention. As they are exemplified, it is possible to cite Williamson reaction, in which it is obtained by treating a fluorine-containing alcohol with an alkali metal, followed by a reaction with an allyl halide. As the alkali metal thereupon, it is possible to use various alkali metal compounds, such as sodium hydride, potassium hydride, sodium hydroxide, and potassium hydroxide. The halogen of the allyl halide is exemplified by fluorine, chlorine, bromine and iodine. Allyl chloride, allyl bromide or allyl iodide is cited as a preferable one, since reactivity is good and since the target allyl ether is obtained efficiently.

[0012]

It is possible to use a solvent upon the reaction. They are not particularly limited, as long as they do not interfere with the target reaction. There is preferable one, such as tetrahydrofuran, diethyl ether and dimethylformamide, which is low in reactivity with the alkali metal compound. Although the temperature upon synthesis is not particularly limited, a range of –30℃ to +100℃ is desirable due to reactivity and handling easiness. More preferably, it is a range of –10℃ to +80℃. Separation and purification of the reaction product may be conducted by general methods. As they are exemplified, there are cited concentration, extraction, distillation,

recrystallization, filtration, and column chromatography. These may be combined together.

[0013]

A novel fluorine-containing allyl ether of the present invention can be copolymerized with monomers, such as α-trifluoromethyl acrylic esters and acrylic esters, that are useful for resist resins. Furthermore, the obtained fluorine-containing copolymers are soluble in various organic solvents and are suitable for the coating use. More specifically, it becomes useful as a raw material monomer for base polymers of resists that are low in light scattering and absorption, for producing semiconductors. Furthermore, it becomes useful also as a monomer for base polymers of plastic optical fibers, optical waveguide materials, and optical materials such as anti-reflection film materials.

[0014]

[Embodiments of the Invention]

Next, the present invention is explained in more detail by examples; however, the present invention is not limited at all to these.

[0015]

[Examples]

[Example 1] Synthesis of Allyl Ether 1

A 300mL glass container was charged with 29.2g of an alcohol 1 represented as follows, 14.5g of allyl bromide, and 100mL of dry dimethylformamide. While it was stirred under cooling in a water bath, the inside of the container was replaced with nitrogen. Then, 6.0g of 60% sodium hydride were gradually added to the container under nitrogen stream. After stirring for 30min, 30cc of water were gradually added to the container, and the reaction was terminated. An organic matter was extracted from the reaction mixture liquid with diethyl ether, followed by washing with saturated brine, drying with anhydrous magnesium sulfate, distilling the solvent off, and distillation under reduced pressure, thereby obtaining 30.2g of the target allyl ether 1 represented as follows. The ally ether 1 is a mixture of two kinds of

stereoisomers. The obtained compound was identified by nuclear magnetic resonance and mass spectroscopy.

Properties Data

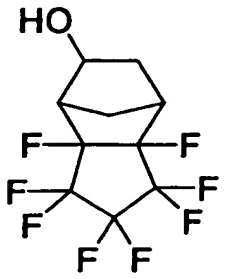
^{1}H NMR ($CDCl_3$, TMS standard, 400MHz)

δ 1.6-1.7 (m, 2H), 2.0-2.4 (m, 2H), 2.8-3.0 (m, 2H), 3.8-4.0 (m, 3H), 5.2-5.3 (m, 2H), 5.8-5.9 (m, 1H)

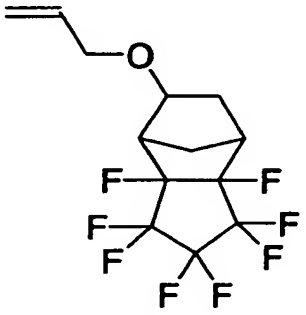
MS m/z (%) 322 (M+, 100), 239 (36), 95 (45)

[0016]

[Chem. 5]



Alcohol 1



Allyl ether 1

[0017]

[EXAMPLE 2] Synthesis of Allyl Ether 2

A 300mL glass container was charged with 41.6g of an alcohol 2 represented as follows, 14.5g of allyl bromide, and 100mL of dry dimethylformamide. While it was stirred under cooling in a water bath, the inside of the container was replaced with nitrogen. Then, 6.0g of 60% sodium hydride were gradually added to the container under nitrogen stream. After stirring for 30min, 18.2g of the target allyl ether were obtained by operations similar to Reaction Example 1. The obtained compound was identified by nuclear magnetic resonance.

Property Data

^{1}H NMR ($CDCl_3$, TMS standard, 400MHz)

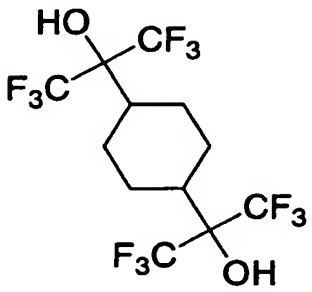
δ 1.6-1.7 (m, 4H), 2.0-2.1 (m, 4H), 2.2-2.3 (m, 2H), 2.94 (s, 1H), 4.27 (d, J= 5.2Hz, 2H), 5.22 (dd, J=1.2, 10.4Hz), 5.31 (dd, J=1.2, 17.0Hz, 1H), 5.8-5.9 (m,

1H)

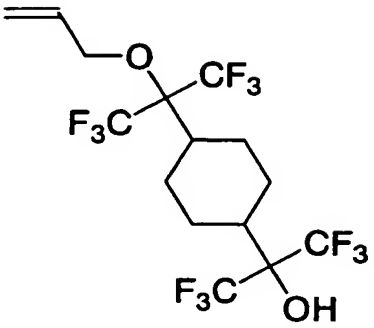
MS m/z (%) 456 (M+, 1), 249 (100), 207 (47)

[0018]

[Chem. 6]



Alcohol 2



Allyl ether 2

[0019]

[Advantageous Effect of the Invention]

A fluorine-containing allyl ether compound of the present invention can be copolymerized with monomers, such as α-trifluoromethyl acrylic esters and acrylic esters, that are useful for resist resins. It becomes useful as a raw material monomer for base polymers of resist materials and optical materials that are low in light scattering and absorption and are soluble in organic solvents.